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Project Summary

Sulfur Dioxide Oxidation Reactions in Aqueous Solutions

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The kinetics and mechanisms of more than one hundred reactions involving the aqueous phase oxidation of sulfur dioxide and nitrogen oxides in mixed catalyst/oxidant systems at pH = 0 to 3 were investigated.

The systems investigated involve different redox reaction types: SO_2/O_2; SO_2/NO_x; SO_2/H_2O_2; SO_2/O_3; NO_x/O_3; NO_x/H_2O_2. The SO_2/O_2 system demonstrated little reactivity unless a catalyst was present. The most effective metal catalysts were FE^{+++} and Mn^{++} with a complex synergism between Fe and Mn.

In the SO_2/NO_x system the nitrite ion caused a rapid reaction producing N_2O. The reaction did show slight inhibition by toluene and hexene, but was unaffected by metal ion catalysts.

The SO_2/H_2O_2 reaction in water is extremely fast and insensitive to catalysis or inhibition.

The SO_2/O_3 reaction is also rapid and similarly insensitive to catalysis or inhibition.

Nitrite oxidation by both ozone and hydrogen peroxide is rapid. The pH dependence of these two reactions was determined.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Our understanding of the atmospheric chemistry of sulfur and nitrogen oxides is important for establishing control strategies both for the primary pollutants, sulfur dioxide and nitric oxide, and for their aerosol formation products, sulfates and nitrates. Research in the past ten years has identified the importance of several gas phase reactions leading to sulfate or nitrate formation. It is only recently that liquid droplet phase mechanisms have been addressed as a possible explanation for the wintertime presence of sulfate and nitrate in regions where photochemical oxidant potential is obviously low.

This project has addressed, in a systematic fashion, over one hundred aqueous phase reactions of potential significance in sulfate and nitrate formation. Environmentally important metal catalysts, commonly found oxidants (O_2, O_3, H_2O_2) in the ambient air, and potential inhibitors or accelerators of the main reactions, $SO_2 \rightarrow SO_4^=$ and $NO_x \rightarrow NO_3^-$ were studied for their reaction rates.

Procedure

The apparatus used consisted of an ultraviolet light source, a Durrum D-103 stopped flow system, monochromator (PAR 1208) and two detection systems interfaced to a minicomputer. The detection systems used, depending on reactions conditions, were (1) a PAR 1205D Silicon Intensified Target Detector linked to a PAR 1205A Optical Multichannel Analyzer and (2) an RCA IP28 phototube maintained at -650v by a Fluke 405 Power Supply. The tube is linked to a Biomation 302 Transient Recorder to record waveshape during selected periods of time. The minicomputer used was

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Fresh aqueous solutions were prepared daily using 18 megohm resistivity water obtained from a Milli-Q water purification system. HCl was used to maintain a pH of less than 4. The pH was measured before each run using an Orion 701A digital ionalyzer. The water for the SO_2 solutions was deoxygenated by passing a steady flow of nitrogen through it. For the ozone reactions an Orec Model 03V5-0 ozonator was used to prepare 1×10^{-4}M solutions. The reductant is placed on one side of the stopped flow system while the oxidant plus catalysts or inhibitors is placed on the other. The capability to detect 1×10^{-5}M of the absorbing species existed; usually solutions were prepared at concentrations of 1×10^{-3}M to 1×10^{-4}M to obtain a better signal to noise ratio.

Results

The following rate expressions have been determined during the course of this project:

(1) For the $SO_2 + O_2$ reaction at pH = 2

$$d(S_{VI})/dt = 1970\,(Mn^{++}) + 82(Fe^{+++})\left[1 + \frac{2.67\times10^{3}(Mn^{++})^{1.5}}{6.31\times10^{-6}+(Fe^{+++})}\right](S_{IV})$$

The reaction is zeroth order in O_2.

(2) For the $SO_2 + NO_2^-$ reaction:

$$d(S_{VI})/dt = 142(H^+)^{1/2}\,(HNO_2+NO_2^-)\,(SO_2{\cdot}Aq+HSO_3^-)$$

(3) For the $SO_2 + H_2O_2$ reaction:

$$d(S_{VI})/dt = \frac{7.2\times10^{4}(H_2O_2)(SO_2{\cdot}Aq)}{0.1+(H^+)} = \frac{4.5\times10^{6}(HSO_3^-)(H_2O_2)(H^+)}{0.1+H^+}$$

(4) For the $SO_2 + O_3$ reaction:

$$d(S_{VI})/dt = \frac{1.9\times10^{4}(SO_2{\cdot}Aq+HSO_3^-)(O_3)}{(H^+)^{1/2}}$$

(5) For the $NO_2^- + O_3$ reactions:

$$\frac{-d(O_3)}{dt} = \frac{200(O_3)(HNO_2+NO_2^-)}{(H^+)}$$

(6) For the $NO_2^- + H_2O_2$ reaction:

$$\frac{-d(N_{III})}{dt} = 4.6\times10^{3}(N_{III})(H_2O_2)(H^+)$$

Conclusions

Of the six reaction rate expressions listed in the Results section, the $SO_2 + H_2O_2$ reaction appears the most likely to be significant in the atmosphere when acidic aerosols are present, but any of the six can become important under certain conditions. For example, the Fe/Mn synergistic effect may be the predominant pathway to sulfate formation in a coastal urban environment during wintertime conditions.

As previously stated the $SO_2 + H_2O_2$ appears to be the most significant of those studied. At low pH (0 to 3) the reaction is faster than one might expect from a straight line extrapolation of the higher pH data obtained by others. The peroxide reaction was found to be insensitive to catalysis or inhibition by Fe^{+++}, Mn^{++}, toluene, pinene, hexene or hydroquinone.

The temperature dependence of the $SO_2 + H_2O_2$ reaction was determined and the conclusion was that the relatively low activation energy for the kinetics leads to a net increase in the atmospheric rate as the temperature is lowered because of the increasing Henry's Law constants for SO_2 and H_2O.

Estimates of the atmospheric oxidation rate for 1 ppb H_2O_2 in the gas phase and in a typical cloud are on the order of 2% min^{-1} for SO_2, which is higher than any reported rates, and as high as the rate allowed by the heterogeneous reactivity of SO_2 with droplet surfaces.

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H. Barnes is the EPA Project Officer (see below).
The complete report, entitled "Sulfur Dioxide Oxidation Reactions in Aqueous Solution," (Order No. Pb 81-196 834; Cost: $6.50, subject to change) will be available only from:
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